

# **ELECTROLYTE SOLUTION FOR MANUFACTURING ELECTROLYTIC COPPER FOIL AND ELECTROLYTIC COPPER FOIL MANUFACTURING METHOD USING THE SAME**

## **5 BACKGROUND OF THE INVENTION**

This application claims the priority of Korean Patent Application No. 2002-70802 filed on 14 November 2002 in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

## **10 FIELD OF THE INVENTION**

The present invention generally relates to an electrolyte solution used to manufacture an electrolytic copper foil for a printed circuit and an electrolytic copper foil for an electrode collector of a secondary battery, the electrolytic copper foil using the same, and an electrolytic copper foil manufacturing method  
15 thereof.

## **SUMMARY OF THE INVENTION**

A printed circuit board using the electrolytic copper foil is widely used as a precise control circuit of various electric, electronic communication apparatuses such as radios, TVs, computers, telephone exchanges, wireless transceivers, etc.  
20 Recently, as a degree of integration of the printed circuit board increases, circuits of the board get minute and multilayered. Particularly, the electrolytic copper foil is highly demanded in terms of COF (Chip On Flex) and TAB (Tape Automatic Bonding) aspects, and is broadly used as an electrode collector of a secondary battery by improving its physical properties.

25 Generally, the electrolytic copper foil is created by electrolytic methods, and is manufactured from a cylinder-shaped cathode (also, called a drum) consisting of titanium, an anode consisting of a lead alloy keeping certain intervals or titanium covered by an iridium oxide, and an electrolytic cell including an electrolyte solution and current power. The electrolyte solution is  
30 composed of sulfuric acid and/or a copper sulfate. When DC flows between the cathode and the anode as rotating the cylinder-shaped cathode, copper is electrodeposited on the cathode, thereby consecutively producing the electrolytic copper foil. Thus, a process of restoring a copper ion to metal with the electrolytic

methods is called a thin film process.

Next, when necessary, to improve an adhesive force with an insulating substrate, the copper foil obtained from the thin film process can pass through additional surface treatment processes including a roughness treatment process (also, called a nodule treatment process), a nonproliferation process to prevent the copper ion from being proliferated, an anticorrosive process to prevent oxidation from outside, a chemical adhesive force improving process to complement an adhesive force with the insulating substrate, and so on. If passing through the surface treatment process, the copper foil is made for a low profile printed circuit. And, if only an anticorrosive process of the surface treatment process is performed, the copper foil is made for the secondary battery.

In case the electrodeposited copper foil is used for the printed circuit, the copper foil is supplied to a PCB (Printed Circuit Board) process manufacturer while being adhered (laminated) to the insulating substrate after the surface treatment process. However, if used for the secondary battery, the copper foil is supplied to a secondary battery manufacturer via the anticorrosive process only.

For the copper foil appropriate for a minute and highly integrated PCB circuit, the surface of the copper foil contacted with the insulating substrate should have a small roughness. In addition, while coupling the electrolytic copper foil with the insulating substrate, if the copper foil gets stress by thermal expansion or heat-shrink and moreover, the copper foil is laminated in multilayer way, it may have scratches due to friction with a neighboring copper foil. More seriously, the copper foil can be exfoliated from the insulating substrate or have circuit damage, or a PCB may get bent or distorted. To protect the copper foil from these problems, it is necessary to have a proper elongation without suddenly deteriorating mechanical intensity at high temperature. When the electrolytic copper foil is used as the collector for the secondary battery, electrode materials should cover both sides of the copper foil. In this case, if both sides of the electrolytic copper foil have a different roughness, battery characteristics differ from each side. Therefore, it is required to have the same or a similar roughness on both sides of the electrolytic copper foil. Furthermore, to reduce weight and a manufacturing cost of the battery and increase energy density of the battery, the

electrolytic copper foil should be manufactured in thin type. Even though the copper foil is thin, it is necessary to have sufficient mechanical intensity and an elongation at high temperature, without being bent in a future treatment process.

To satisfy the above requirements, the prior art has suggested a method of making an electrolytic copper foil by adding various organic additives to an electrolyte solution. As a representative example, the United States Patent No. 5,431,803 has been suggested to lower a surface roughness, providing a method of manufacturing an electrolytic copper foil that maintains concentration of a chlorine ion less than 1 mg in a 1-liter electrolyte solution. However, the electrolytic copper foil manufactured by a technology suggested in the United States Patent No. 5,431,803 has 61 kgf/mm<sup>2</sup> to 84 kgf/mm<sup>2</sup> of mechanical intensity at room temperature as well as 17 kgf/mm<sup>2</sup> to 25 kgf/mm<sup>2</sup> at 180°C, and has about 6μm of the maximum value of the surface roughness: Rmax for a surface treatment. Thus, it is not appropriate for the secondary battery. Also, it is difficult to carry out a consecutive operation as maintaining the concentration of the chlorine ion less than 1 mg in the electrolyte solution.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an electrolyte solution for a printed circuit, an electrolytic copper foil produced using the same, and a manufacturing method thereof for controlling a roughness on both sides of the electrolytic copper foil in the same or similar way according to electrolyte solution additives and for preventing sudden intensity changes even at high temperature compared to room temperature by controlling the amount of the electrolyte solution additives.

It is another object of the present invention to provide an electrolyte solution used to manufacture an electrolytic copper foil, the electrolytic copper foil produced using the same, and an electrolytic copper foil manufacturing method thereof for having a roughness Rz value of a rough surface is less than 2.0 μm in a thin film state and for preventing sudden intensity changes even at high temperature compared to room temperature.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

To accomplish the above objects, as an electrolyte solution for manufacturing an electrolytic copper foil, the present invention provides the electrolyte solution, the electrolytic copper foil produced by using the electrolyte solution, and an electrolytic copper foil manufacturing method thereof. In an electrolyte solution containing at least selected one of sulfuric acid and copper sulfate used to manufacture an electrolytic copper foil by electrolysis, the electrolyte solution for manufacturing the electrolytic copper foil, based on the 1-liter electrolyte solution, comprising: 0.5 to 40 mg of at least one sulfur compound selected from a disulfur compound, dialkylamino- T-oxomethyl- thioalkan sulfonic acid, and thioalkan sulfonic acid salt; 1 to 1000 mg of at least more than one kind of an organic compound selected from a group consisting of a poly akylene glycol-type surfactant and low molecular gelatin; and 0.1 to 80 mg of chlorine ion added.

A solution comprising i) sulfuric acid and copper salt rather than copper sulfate, or ii) copper sulfate and acid rather than sulfuric acid may be also used as the electrolyte.

The organic compound comprising low molecular gelatin without polyalkylene gulycol type surfactant may be also used as the organic compound.

Generally, a process of manufacturing an electrolytic copper foil for a printed circuit is divided into a thin film process and a surface treatment process.

The thin film process is generally performed by using an electroforming cell. Within an electrolytic cell, a semi-cylinder type anode and a cylinder-type rotating cathode are located at certain intervals, and the electrolyte solution is consecutively supplied between the anode and the cathode. By flowing DC between the anode and the cathode, a copper ion of the electrolyte solution is restored to metal having predetermined thickness from the cathode. Next, a copper foil (undisposed) that does not pass through a future treatment process is exfoliated from the surface of the cathode. A lead alloy is widely used for the anode, but recently, intervals are changed by corrosion of a lead oxide. Therefore, titanium covering an iridium oxide is more used. The cathode is used by plating

iron with chromium, however recently, stainless materials are covered with titanium to lengthen the span of life.

Next, to provide requested characteristics when necessary, an additional treatment process of passing the undisposed copper foil through a processor can be performed. This treatment process includes a roughness treatment process to improve an adhesive force when laminated on an insulating substrate, a nonproliferation process to prevent a copper ion from being proliferated, and an anticorrosive process to prevent oxidation during storage, transportation or a lamination forming process of the copper foil and the insulating substrate. Hereinafter, the above processes will be more fully described. The above processes are performed in the processor having the anode, and a surface treatment copper foil is finally obtained through these processes.

The electrolyte solution supplied between the anode and the cathode is a copper sulfate solution, and its blending based on 1 liter is as follows:

Copper concentration is between 50g and 110g, and desirably, between 60g and 100g. Sulfuric acid concentration is between 80g and 200g, and desirably, between 90g and 120g. Temperature of the electrolyte solution is between 40 °C and 80 °C. Current density is between 400A/cm<sup>2</sup> and 10000A/dm<sup>2</sup>, and desirably, between 50A/dm<sup>2</sup> and 85A/dm<sup>2</sup>. If the copper concentration is less than 50g, the surface of an electrodeposited copper foil is rough and powder is formed, lowering productivity. However, if more than 110g, the electrolyte solution is crystallized, deteriorating working efficiency. If the sulfuric acid concentration is less than 80g, an electrolytic voltage rises, resulting in an increase of production cost. Also, temperature of the electrolyte solution rises, causing deterioration of mechanical intensity of the copper foil. If the sulfuric acid concentration is more than 200g, the electrolyte solution is highly apt to be corrosive even though the electrolytic voltage lowers, thereby quickly corroding an electrode electrolyzing the copper foil.

At this time, the electrolyte solution contains a sulfur compound having 0.5 to 40 mg of concentration and at least more than one kind of an organic compound selected from a group consisting of a poly alkylene glycol-type surfactant having 1 to 1000 mg of concentration and low molecular gelatin as

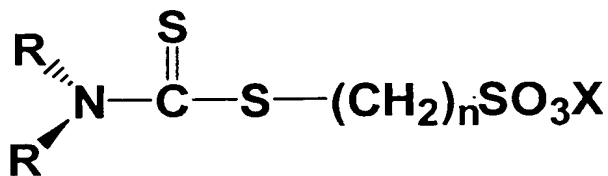
additives. In addition, a chlorine ion having a range of 0.1 mg to 80 mg is added.

More desirably, to increase intensity of the electrolytic copper foil produced by the electrolyte solution, it is possible to use a nitrogen compound. For a thiourea derivative, which is the nitrogen compound, IM(2-imidazolidinethione) is used within a range of 0.1 mg to 8 mg. As for the polyalkylene glycol-type surfactant, it is available to use poly ethylene-type, poly propylene-type, and poly butylenes-type surfactants. Particularly, poly ethylene glycol can be representative of the poly ethylene-type surfactant.

A disulfur compound and dialkylamino- T-oxomethyl- thioalkan sulfonic acid or thioalkan sulfonic acid salt are included in the sulfur compound. The disulfur compound includes SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt)), and dialkylamino- T-oxomethyl- thioalkan sulfonic acid or salt thereof can contain dithiocarbamic acid or salt thereof, and DPS (N, N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) is representative.

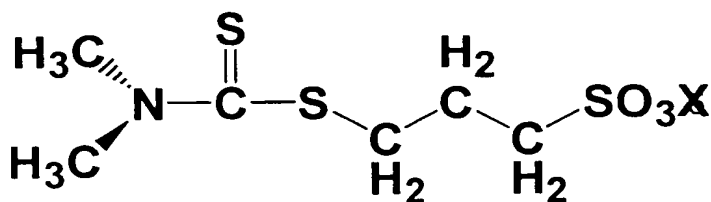
A formula of the dialkylamino- T-oxomethyl- thioalkan sulfonic acid or the salt thereof is shown in a chemical formula 1, and a formula of the DPS as a representative example is shown in a chemical formula 2, then a formula of the SPS is shown in a chemical formula 3.

#### Chemical formula 1

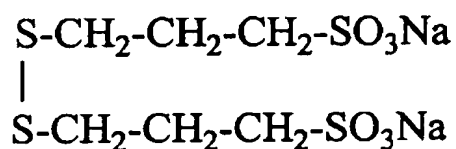


‘R’ in the chemical formula 1 means an alkyl group (carbon atom 1~6), ‘n’ is 2 ~ 3 (ethane , propane), and ‘X’ means hydrogen atom or alkali metal atom.

**Chemical formula 2**



**Chemical formula 3**



10

Among the above additives, the roles of the sulfur compound and the surfactant are very important, since these compounds give direct influence on a surface roughness and tensile strength. Compared to a general electrolytic copper foil added with glue or gelatin, the sulfur compound generally has a small size of grains and functions as a grain refiner or a brightener. The added surfactant functions as a carrier or an electrodeposition leveler lowering a surface roughness of a mat surface of the electrolytic copper foil, influencing electroposition. In this case, the surfactant is absorbed into a protruded part of an electrode surface as carrying the sulfur compound, which is a brightener, to a cathode surface, and suppresses growth of the protruded part, thereby interrupting the growth firstly. And the sulfur compound, which is the grain refiner, firstly functions in a minute valley part of an electroposition surface, and enables a copper ion to be restored and grow up in this part first of all, thereby controlling a roughness of the electrodeposition surface.

25

The thiourea derivative, the nitrogen compound used in the present invention suppresses crystal growth of copper at room temperature or high temperature by eutectoid-processing nitrogen on an electrodeposition layer, and also restrains strength deterioration. Thus, when the nitrogen compound, the thiourea derivative is added, it is possible to prevent the strength deterioration, which occurs otherwise. So, a defective proportion caused when dealing with the electrolytic copper foil or manufacturing the printed circuit can be reduced. Moreover, the strength can be changed by controlling an amount of the additives, thereby adjusting physical properties of the electrolytic copper foil.

For the electrolytic copper foil in accordance with the present invention, if it is undisposed, it seems that a roughness of a rough surface (mat surface) has an Rz value having a range of 2.0  $\mu\text{m}$ . Rz has been measured by an IPC TM 650 2.2.17A method. For other copper foil passing through surface treatment, it seems that the roughness of the rough surface (mat surface) has an Rz value having a range of 1.0 ~ 3.5  $\mu\text{m}$ . Since a roughness value of a drum surface (bright surface) of the copper foil contacted with the drum surface is produced according to polishing of the drum surface, there is no particular restriction.

In order to improve an adhesive force with an insulating substrate, if necessary, the above undisposed copper foil can pass through additional surface treatment processes including a roughness treatment process (also, called a nodule treatment process), a nonproliferation process to prevent a copper ion from being proliferated, and an anticorrosive process to prevent oxidation from outside. If passing through the surface treatment process, the copper foil is made for a low profile printed circuit, however, if passing through the anticorrosive process only, the copper foil is for a secondary battery.

The roughness treatment process consists of two steps or three steps. In a first step, a core of minute powder is made, and the powder is coupled with the copper foil in a second step because the powder does not have an adhesive force with the copper foil. In a third step, a minute protrusion is given to the coupled powder again. The first step is as follows. Based on a 1-liter electrolyte solution, copper concentration is between 10g and 40g, and desirably, between 15g and 25g. Sulfuric acid concentration is between 40g and 150g, and desirably between



60g and 100g, and temperature of the electrolyte solution is between 20 °C and 40 °C.

Current density is between 20A/dm<sup>2</sup> and 100A/dm<sup>2</sup>, and desirably, between 40A/dm<sup>2</sup> and 80A/dm<sup>2</sup>. The second step is as follows. Copper concentration is between 50g and 110g, and desirably, between 55g and 100g. Sulfuric acid concentration is between 80g and 200g, and desirably, between 90g and 120g. Temperature of the electrolyte solution is between 40 °C and 80°C. Current density is between 20A/dm<sup>2</sup> and 100A/dm<sup>2</sup>, and desirably, between 40A/dm<sup>2</sup> and 80A/dm<sup>2</sup>. The nonproliferation process is as follows. To prevent the copper ion from being proliferated, a barrier layer is formed with various single metal such as zinc, nickel, iron, cobalt, molybdenum, tungsten, tin, indium, and chrome, or with 2 or 3 kinds of alloys.

Then, to prevent oxidation during storage, transportation, or a lamination forming process of the copper foil and the insulating substrate, the anticorrosive process is carried out. The anticorrosive process performs chromate passivation with chromic acid, sodium dichromate, potassium dichromate, chromic anhydride, etc. Next, a process for increasing chemical cohesion is executed.

Also, a chemical adhesive force improving process can be carried out to complement an adhesive force with the insulating substrate. For this, there are usable adhesion accelerators such as a silane coupling agent (RSiX<sub>3</sub>), silicon peroxygen (R<sub>4-n</sub>Si(OOR')<sub>n</sub>), a chromium-based adhesion accelerator ((RCO<sub>2</sub>H<sub>3</sub>OHCrOHCrHOH<sub>2</sub>)<sub>2</sub>OH), an organic titanium based adhesion accelerator ((C<sub>4</sub>H<sub>9</sub>CHC<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>4</sub>Ti), an organic phosphate based adhesion accelerator (RO<sub>2</sub>P(OH)<sub>2</sub>), and others.

## **Embodiments**

Hereinafter, the present invention will be described in reference to the embodiments and compared examples. Here, a symbol 'g/L' means a content of a corresponding material based on a 1-liter electrolyte solution.

For a thin film process, the electrolyte solution having blending like described in Table 1 is prepared. Copper concentration of the electrolyte solution is 80 g/L, sulfuric acid concentration is 90 g/L, and temperature of the electrolyte solution is 45 °C. Additives like described in Table 1 have been added. Current

density was electrodeposited in  $60\text{A/dm}^2$ , and chlorine ion was maintained in  $25\text{mg/L}$ .

For embodiment 1,  $6\text{ mg/L}$  of DPS (N, N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and  $1\text{mg/L}$  of  
5 PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

For embodiment 2,  $1\text{mg/L}$  of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) was used as a sulfur compound, and  $30\text{mg/L}$  of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

For embodiment 3,  $30\text{ mg/L}$  of DPS (N, N-Dimethyldihiocarbamic acid  
10 (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and  $30\text{ mg/L}$  of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

For embodiment 4,  $5\text{ mg/L}$  of SPS (Bis-(3-sulfopropyl)-disulfide, disodium salt) was used as a sulfur compound, and  $1\text{ mg/L}$  of PEG (Poly Ethylene Glycol) was used as a poly alkylene glycol-type surfactant.

15 For embodiment 5,  $3\text{ mg/L}$  of DPS (N, N-Dimethyldihiocarbamic acid (3-sulfopropyl) ester, sodium salt) was used as a sulfur compound, and  $800\text{ mg/L}$  of PPG (Poly Propylene Glycol) and  $5\text{ mg/L}$  of low molecular gelatin less than molecular weight  $6000$  were added as a poly ethylene glycol surfactant.

For embodiment 6,  $5\text{ mg/L}$  of SPS (Bis-(3-sulfopropyl)-disulfide,  
20 disodium salt) was used as a sulfur compound,  $0.5\text{ mg/L}$  of IM (2-imidazolidinethione), which was a thiourea derivative, was as a nitrogen compound, and  $25\text{ mg/L}$  of PEG (Poly Ethylene Glycol) was used as a poly ethylene glycol-type surfactant.

For embodiment 7,  $3\text{ mg/L}$  of SPS (Bis-(3-sulfopropyl)-disulfide,  
25 disodium salt) and  $5\text{ mg/L}$  of DPS (N, N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt) were as a sulfur compound, and  $30\text{ mg/L}$  of PEG (Poly ethylene glycol) and  $30\text{ mg/L}$  of PPG (Poly Propylene Glycol) were used as a poly ethylene glycol-type surfactant.

By using the electrolyte solution prepared like above, a titanium anode  
30 covering an iridium oxide, and a rotating cylinder-type titanium cathode, the undisposed copper foil corresponding to the embodiments 1 to 7 was obtained, respectively, under an electrolytic condition like described in Table 1.

In case of the sulfur compound, an Rz value tended to exceed 2.0  $\mu\text{m}$  by an increase of a surface roughness of a rough surface in a range of exceeding 40 mg/L. When used less than 0.5 mg/L, the surface roughness did not lower, rather the roughness increased as lowering an elongation. As for the poly ethylene glycol-type surfactant, it was possible to confirm a function of lowering the surface roughness of the rough surface within a range of 1 mg/L to 1000 mg/L. More desirably, a desirable surface roughness could be obtained within a range of 1 mg/L to 300 mg/L. However, in this case, it was required to control using current density in higher or lower way according to its amount. For the sulfur compound and the poly ethylene glycol-type surfactant, if concentration was higher than an upper limit above, the surface got rough and burning phenomenon (electrodeposited into powder) occurred. Thus, they might not be usable for manufacturing a satisfactory electrolytic copper foil.

So as to control hardness of the manufactured electrolytic copper foil, it was proper to have a range of 0.1 mg/L to 8 mg/L for the nitrogen compound additionally included to form the electrolyte solution. If an amount of an additive was too little, the hardness got slightly improved, and if too much, the hardness got higher but a surface roughness rose, thereby lowering an elongation.

For each of the undisposed copper foil, a surface roughness Rz was measured according to an IPC TM 650 2.2.17A method, and an elongation and tensile strength of the copper foil have been measured at room temperature (25 °C) and 180 °C according to an IPC TM 650 standard processing method. The results are shown in Table 2.

Next, a surface treatment process was carried out for the undisposed copper foil in accordance with the embodiments 1 to 7. First, for a nonproliferation process, 110 g/L of sodium cyanide, 60 g/L of sodium hydroxide, 90 g/L of copper cyanide, and 5.3 g/L of zinc cyanide have been electrodeposited with pH 11.0 to 11.5 at 50 °C, having 5A/dm<sup>2</sup> of current density for 10 seconds. For an anticorrosive process, 10 g/L of sodium dichromate has been measured with pH 4.5, having 0.5A/dm<sup>2</sup> of current density for 2 seconds.

### Compared Examples

The composition of the electrolyte solution and the chlorine ion concentration are the same as the above embodiments. For a compared example 1, 2 mg/L of low molecular gelatin less than 6000 molecular weight has been added as an additive. For a compared example 2, 1 mg/L of TU (thiourea) has been added with 2 mg/L of low molecular gelatin less than 6000 molecular weight. For a compared example 3, 50 mg/L and 30 mg/L of SPS and PEG, respectively, have been added. And for a compared example 4, 3 mg/L and 1500 mg/L of DPS and PPG, respectively, have been added.

Under the electrolytic condition described in Table 1, the undisposed copper foils corresponding to the compared examples 1 to 4 have been obtained, as well as a surface roughness Rz for the undisposed copper foils, and an elongation and tensile strength were measured at room temperature (25 °C) and 180 °C by an IPC IM 650 2.4.18A method. The results are shown in Table 2. Next, a surface treatment process has been carried out for the undisposed copper foils in accordance with the compared examples 1 to 4.

Table 2 shows the results of comparing physical properties of the copper foil tentatively manufactured through the embodiments and the compared examples under the condition suggested in Table 1.

Like displayed in Table 2, according to the embodiments in accordance with the present invention, a roughness (Rz) of a rough surface is controlled less than 2.0 by the sulfur compound. Thus, it is possible to maintain similarly to a roughness (Rz) of a drum surface and change strength by controlling an amount of the thiourea derivative, the nitrogen compound, thereby enabling the electrolytic copper foil to be manufactured for various purposes.

**Table 1**

|                               | Additives         |                   |                  |                   |                   |                                       |                  | Solution Composition |                         |                         |
|-------------------------------|-------------------|-------------------|------------------|-------------------|-------------------|---------------------------------------|------------------|----------------------|-------------------------|-------------------------|
|                               | SPS<br>(mg/<br>L) | DPS<br>(mg/<br>L) | IM<br>(mg/<br>L) | PEG<br>(mg/<br>L) | PPG<br>(mg/<br>L) | Low<br>Molecular<br>Gelatin<br>(mg/L) | TU<br>(mg/<br>L) | Cl-<br>(mg/<br>L)    | Copper<br>(g/L:<br>Ion) | Sulfur<br>Acid<br>(g/L) |
| <b>Embodiment 1</b>           | -                 | 6                 | -                | 1                 | -                 | -                                     | -                | 25                   | 80                      | 90                      |
| <b>Embodiment 2</b>           | 1                 | -                 | -                | 30                | -                 | -                                     | -                |                      |                         |                         |
| <b>Embodiment 3</b>           | -                 | 30                | -                | 30                | -                 | -                                     | -                |                      |                         |                         |
| <b>Embodiment 4</b>           | 5                 | -                 | -                | 1                 | -                 | -                                     | -                |                      |                         |                         |
| <b>Embodiment 5</b>           | -                 | 3                 | -                | -                 | 800               | 5                                     | -                |                      |                         |                         |
| <b>Embodiment 6</b>           | 5                 | -                 | 0.5              | 25                | -                 | -                                     | -                |                      |                         |                         |
| <b>Embodiment 7</b>           | 3                 | 5                 | -                | 30                | 30                | -                                     | -                |                      |                         |                         |
| <b>Compared<br/>Example 1</b> | -                 | -                 | -                | -                 | -                 | 2                                     | -                |                      |                         |                         |
| <b>Compared<br/>Example 2</b> | -                 | -                 | -                | -                 | -                 | 2                                     | 1                |                      |                         |                         |
| <b>Compared<br/>Example 3</b> | 50                | -                 | -                | 30                | -                 | -                                     | -                |                      |                         |                         |
| <b>Compared<br/>Example 4</b> | -                 | 3                 | -                | -                 | 1500              | -                                     | -                |                      |                         |                         |

Current density: 60 A/dm<sup>2</sup>, Solution temperature: 45 °C

DPS: N-Dimethyldithiocarbamic acid (3-sulfopropyl) ester, sodium salt

5 SPS: Bis-(3-sulfopropyl)-disulfide, disodium salt

IM: 2-imidazolidinethione

PEG: Poly Ethylene Glycol

PPG: Poly Propylene Glycol

Low molecular gelatin: gelatin less than 6000 molecular weight

10 TU: thiourea

**Table 2**

|                               | <b>Surface<br/>Roughness<br/>of Rough<br/>Surface</b> | <b>Surface<br/>Roughness<br/>of Drum<br/>Surface</b> | <b>Tensile<br/>Strength<br/>(Room<br/>Temperature)</b> | <b>Elongation<br/>(Room<br/>Temperature)</b> | <b>Tensile<br/>Strength<br/>(180 °C)</b> | <b>Elongation<br/>(180 °C)</b> |
|-------------------------------|---|--|--|--|--|--------------------------------|
|                               | <b>(Rz:μm)</b>  | <b>(Rz:μm)</b>                                       | <b>(kgf/mm<sup>2</sup>)</b>                            | <b>(%)</b>                                   | <b>(kgf/mm<sup>2</sup>)</b>              | <b>(%)</b>                     |
| <b>Embodiment<br/>1</b>       | <b>1.52</b>   | <b>1.68</b>  | <b>33.2</b>  | <b>8.9</b>                                   | <b>22.5</b>                              | <b>7.6</b>                     |
| <b>Embodiment<br/>2</b>       | <b>1.83</b>   | <b>1.76</b>  | <b>29.5</b>  | <b>9.6</b>                                   | <b>20.9</b>                              | <b>8.0</b>                     |
| <b>Embodiment<br/>3</b>       | <b>1.42</b>   | <b>1.84</b>  | <b>33.4</b>  | <b>12.9</b>                                  | <b>22.2</b>                              | <b>14.4</b>                    |
| <b>Embodiment<br/>4</b>       | <b>1.88</b>   | <b>1.91</b>  | <b>30.4</b>  | <b>12.9</b>                                  | <b>20.6</b>                              | <b>10.6</b>                    |
| <b>Embodiment<br/>5</b>       | <b>1.81</b>   | <b>1.79</b>  | <b>31.4</b>  | <b>4.1</b>                                   | <b>18.4</b>                              | <b>3.1</b>                     |
| <b>Embodiment<br/>6</b>       | <b>0.50</b>   | <b>1.75</b>  | <b>33.2</b>  | <b>11.4</b>                                  | <b>23.6</b>                              | <b>6.0</b>                     |
| <b>Embodiment<br/>7</b>       | <b>1.14</b>   | <b>1.55</b>  | <b>32.0</b>  | <b>8.8</b>                                   | <b>20.6</b>                              | <b>4.2</b>                     |
| <b>Compared<br/>Example 1</b> | <b>3.53</b>   | <b>1.81</b>  | <b>37.1</b>  | <b>5.6</b>                                   | <b>22.8</b>                              | <b>2.2</b>                     |
| <b>Compared<br/>Example 2</b> | <b>1.9</b>  | <b>1.85</b>  | <b>49.0</b>  | <b>1.5</b>                                   | <b>22.0</b>                              | <b>1.9</b>                     |
| <b>Compared<br/>Example 3</b> | <b>2.23</b>   | <b>1.88</b>  | <b>34.2</b>  | <b>1.9</b>                                   | <b>22.2</b>                              | <b>3.5</b>                     |
| <b>Compared<br/>Example 4</b> | <b>2.38</b>   | <b>1.79</b>  | <b>13.9</b>  | <b>0.23</b>                                  | <b>16.9</b>                              | <b>1.2</b>                     |

Like shown in the embodiments 1 to 7 suggested in Table 2, the  
5 electrolytic copper foil manufactured in the embodiments in accordance with the  
present invention has a surface roughness Rz value of a rough surface within a  
range of 2.0 μm in a thin film state. It is also confirmed that tensile strength at

room temperature is not rapidly changed even at high temperature (180 °C) as well.

## RESULTS OF THE INVENTION

An electrolytic copper foil in accordance with the present invention has a roughness Rz value of a rough surface (mat surface) with a range of less than 2.0  $\mu\text{m}$ , if undisposed. However, if the copper foil passes through a surface treatment process, it has a roughness Rz value of a rough surface (mat surface) within a range of 1.0 ~ 3.5  $\mu\text{m}$ . Therefore, the electrolytic copper foil in accordance with the present invention has a relatively lower roughness on the rough surface, and both sides of the electrolytic copper foil have a similar roughness.

An electrolytic copper foil manufactured in prior art has a problem of rapidly causing strength deterioration at high temperature (180 °C), though good strength is maintained at room temperature. However, the electrolytic copper foil in accordance with the present invention does not show any sudden strength change even at high temperature. Accordingly, the electrolytic copper foil in accordance with the present invention is appropriate for a minute and highly integrated PCB circuit.

Furthermore, when used as a collector for a secondary battery, a more reliable battery characteristic can be obtained, since a roughness on both sides of the electrolytic copper foil is similar. The electrolytic copper foil in accordance with the present invention prevents tensile strength from suddenly deteriorating owing to a temperature rise, having excellent elongation characteristics at room temperature and high temperature. Thus, it would not get bent or distorted in a future treatment process nor generate a short circuit. The electrolytic copper foil in accordance with the present invention is proper to be used as the collector for the secondary battery or a printed circuit board.

It is to be understood that changes and modifications to the embodiments described above will be apparent to those skilled in the art, and are contemplated. It is therefore intended that the foregoing detailed description be regarded as illustrative rather than limiting, and that it be understood that it is the following claims, including all equivalents, that are intended to define the spirit and scope of this invention.